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Fluorescence properties, aluminium ion selective emission changes and self-assemblies of positional isomers of 4-(hydroxyphenylthio) naphthalene-1,2-diones

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ABSTRACT

Three positional isomers namely 4-(hydroxyphenylthio)naphthalene-1,2-dione having the *para*-, *ortho*- or *meta*-hydroxyphenylthio units were synthesized and characterized. The isomer having *para*-hydroxyphenylthio unit showed dual-fluorescence in certain solvents such as dimethylacetamide, which could be tuned to single fluorescence emission by adding methanol. Fluorescence emission intensities of these isomers increased by 5–6-fold on addition of aluminium ions, with an exception being the isomer having the *ortho*-hydroxyphenylthio unit, which showed a two tier change of fluorescence intensity with an initial enhancement followed by a decrease. The fluorescence lifetime decay study in the presence and absence of aluminium ions suggests that at low concentration of aluminium ions exciplex formation took place. Crystal structures of these isomers as well as methanol and dimethylacetamide solvates of *para*-hydroxyphenylthio unit containing isomer were determined. Self-assembling patterns have provided information on the nature of hydrogen bonds contributing to proton transfer.

1. Introduction

Fluorescent compounds possessing specific binding with substrates are used as probes [1–8]. Detection of multiple substrates by a fluorescent compound is of special interest [5,6]. To achieve it, fluorescent compounds with multiple binding sites are in use [7,8]. Quinoidal compounds show fluorescent switching properties [9–11] and selective binding to various ions [12–14]. They play important roles in biology [15–17]. Studies on fluorescence emissions of quinoidal compounds have helped to establish different processes, such as retardation effect of lead (II) ions on electron transfer process between quinones of photosystem II [18] and delayed quinone dependent fluorescence emissions in photosynthetic bacteria [19]. Various quinoidal compounds are bioactive [20]. Fluorescence behaviour of quinones has been explored in nano-materials to develop new materials for analytical purpose [21,22]. On the other hand, hydroxyquinones show dual-fluorescence emissions [23,24]. Dual-fluorescence emissions occur through various mechanisms, but generally occur via a twisted intramolecular charge transfer (TICT) or through a planarised intramolecular charge transfer (PICT) emission [25–36]. Intramolecular hydrogen bonds of 1,2-dihydroxyanthraquinone play an important role in the occurrence of dual-fluorescence emissions [34]. Nature of hydrogen bonded assemblies affects dual-fluorescence emissions of fluorophores connected to a phenol [31]. Thus, hypothetical assemblies between a hydroxyphenyl unit with a 1,2-quinone such as **A**-**B** shown Fig. 1, may generate dual-fluorescence emissions by forming different assemblies formed by interplay of weak interactions. In specific cases of phenol connected to quinoidal compounds may help to form exciplexes through a stacking effect to cause dual-fluorescence emission. With such an anticipation we have chosen three positional isomers of a hydroxyphenylthio tethered naphthoquinone, namely 4-(n-hydroxyphenylthio)naphthalene-1,2-dione (where $n = 4$, **1**; $n = 2$, **2** and $n = 3$, **3**) shown in Fig. 1 to study their fluorescence and self-assembling properties.

2. Materials and methods

2.1. Physical measurements

Infrared spectra (KBr pellets) of solid samples were recorded in the region 4000–400 cm^{-1} on a Perkin–Elmer Spectrum-One FT-IR spectrophotometer. Thermogravimetric analyses were performed

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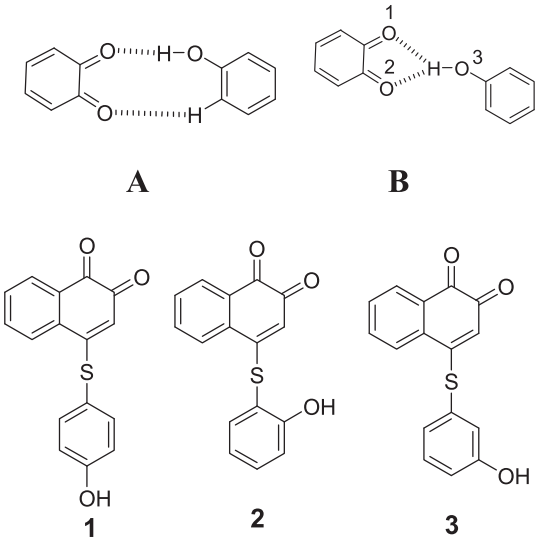

Fig. 1. A-B are representative hydrogen bonded interactions between 1,2-naphthoquinone with phenol and structures of positional isomers **1**–**3**.

on a SDTQ600 thermogravimetric analyzer of TA Instruments, under dry nitrogen atmosphere in the temperature range 30 °C–350 °C with 5 °C per minute heating rate. UV–visible spectra were recorded on a Perkin-Elmer-Lambda 750 UV–visible spectrometer at room temperature. Powder X-ray diffraction data were collected on a Bruker D2 diffractometer in Bragg-Brentano θ–θ geometry with Cu–K_α radiation ($\lambda = 1.5418$ Å) on a glass surface of an air-dried sample using a secondary curved graphite monochromator. Diffraction patterns were collected over a 2θ range of 5–50° at a scan rate 1° min^{-1}. ESI mass spectra were recorded on a micro mass Q-TOF (waters) mass spectrometer by using an acetonitrile/formic acid matrix. Fluorescence emission spectra were recorded on a Perkin–Elmer LS-55 spectrofluorimeter by taking definite amount of each sample and exciting at required wavelength. Fluorescence lifetimes were measured on a picosecond time-resolved cum steady state luminescence spectrometer of Edinburgh instruments, model: FSP920 and LifeSpec II. Quantum yields of fluorescence were determined by using quinine sulphate as a reference in water at room temperature.

$$\text{Quantum Yield} = \frac{\text{Area of the compound}}{\text{Area of Q.S}} \times \frac{\text{Absorbance of Q.S}}{\text{Absorbance of Compound}} \times \frac{\text{R.I of DMA}}{\text{R.I of water}} \times 0.54$$

Here Q.S, DMA and R.I are abbreviations for quinine sulphate, dimethylacetamide and refractive index respectively. Area means the area covered by fluorescence curve of the respective compound.

Binding constants were determined by using the Benesi-Hildebrand equation [37] from changes observed in fluorescence of compounds during fluorescence titrations. For fluorescence titrations 3 mL solution of corresponding compound (either of **1**–**3**) in dimethylacetamide (10^{-5} M) was taken in a quartz cuvette; emission was recorded by exciting at 320 nm. Solution was titrated by adding corresponding solution of metal chloride in dimethylacetamide (10^{-5} M) added in 10 μL aliquot followed by recording emissions.

2.2. Synthesis

Three positional isomers were prepared by following procedure reported earlier by us for analogous compounds [38].

2.2.1. 4-(4-Hydroxyphenylthio)naphthalene-1,2-dione (*1*)

To a well stirred solution of 1,2-naphthoquinone (0.31 g, 2 mmol) in methanol (20 mL) a solution of 4-mercaptophenol (0.25 g, 2 mmol) in methanol (5 mL) was added dropwise. Reaction mixture was stirred at room temperature for 8 h. A red precipitate of **1** was obtained. The precipitate was collected and dried in open air. Crystals of **1** were obtained by slow evaporation of a solution of **1** in dry dimethylformamide. Yield: 92%. IR (KBr, cm^{-1}): 3696 (w), 3502 (bw), 3330 (w), 2967 (w), 2926 (w), 2851 (w), 1701 (w), 1632 (s), 1598 (s), 1577 (m), 1541 (w), 1496 (s), 1480 (m), 1449 (m), 1432 (w), 1345 (s), 1326 (s), 1290 (m), 1257 (m), 1220 (w), 1163 (w), 1115 (w) 1097 (w), 1020 (w), 936 (m), 851 (s), 836 (m), 763 (m), 706 (w), 649 (w), 582 (w). ^{1}H NMR (400 MHz, DMSO-d_6): 10.39 (s, 1H), 8.02 (d, $J = 7.6$ Hz, 1H), 7.94 (d, $J = 7.6$ Hz, 1H), 7.82 (t, $J = 7.2$ Hz, 1H), 7.70 (t, $J = 8$ Hz, 1H), 7.44 (d, $J = 7.2$ Hz, 2H), 6.98 (d, $J = 6.8$ Hz, 2H), 5.55 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 178.6, 175.8, 160.5, 160.1, 137.6, 135.2, 132.6, 131.5, 130.4, 128.6, 124.8, 120.5, 117.5, 113.9, 98.1, 97.9. Mass (ESI) found m/z: 283.0509 ($m + 1$); calculated exact mass for $C_{16}H_{10}O_3S$, 282.0351. UV (methanol) 317 nm ($\varepsilon_{methanol} = 4.71 \times 10^4$ cm^2 mol^{-1}).

2.2.2. 4-(2-Hydroxyphenylthio)naphthalene-1,2-dione (*2*)

To a well stirred solution of 1,2-naphthoquinone (0.31 g, 2 mmol) in methanol (20 mL) a solution of 2-mercaptophenol (0.20 mL, 2 mol) was added drop wise. Reaction mixture was stirred at room temperature for 6 h. A red precipitate obtained was collected by decanting the solvent and dried in open air. Yield: 85%. IR (KBr, cm^{-1}): 3333 (bm), 2828 (w), 2850 (w), 1698 (m), 1631 (s), 1587 (w), 1578 (w), 1528 (m), 1496 (w), 1450 (m), 1347 (m), 1327 (m), 1305 (w), 1295 (m), 1257 (m), 1218 (w), 1174 (w), 1130 (w), 1116 (w), 1063 (w), 972 (m), 938 (m), 866 (w), 850 (m), 836 (w), 778 (s), 754 (m), 709 (w), 661 (w), 502 (w). ^{1}H NMR (400 MHz, DMSO-d_6): 10.34 (s, 1H), 8.02 (d, $J = 7.2$ Hz, 1H), 7.93 (d, $J = 8$ Hz, 1H), 7.73 (d, $J = 8$ Hz, 1H), 7.57 (t, $J = 7.6$ Hz, 1H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.04 (d, $J = 8$ Hz, 1H), 6.88 (t, $J = 7.6$ Hz, 1H), 5.70 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 177.8, 173.6, 162.2, 161.7, 140.1, 138.5, 134.4, 132.9, 131.6, 130.3, 128.5, 125.4, 121.7, 116.1, 99.8, 97.6. Mass (ESI) found m/z: 283.0496 ($m + 1$); calculated exact mass for $C_{16}H_{10}O_3S$, 282.0351. UV (methanol) 316 nm ($\varepsilon_{methanol} = 1.09 \times 10^5$ M^{-1} cm^2).

2.2.3. 4-(3-Hydroxyphenylthio)naphthalene-1,2-dione (*3*)

To a well stirred solution of 1,2-naphthoquinone (0.31 g, 2 mmol) in methanol (20 mL) a solution of 3-mercaptophenol (0.20 mL, 2 mol) was added drop wise. Reaction mixture was stirred at room temperature for 8 h. A red coloured precipitate of compound **3** was formed. Resulting mixture was filtered and dried in open air. Yield: 85%. IR (KBr, cm^{-1}): 3316 (bw), 1687 (m), 1633 (s), 1575 (m), 1525 (s), 1475 (s), 1450 (w), 1325 (s), 1299 (w), 1253 (w), 1226 (s), 1166 (m), 1122 (w), 1019 (m), 955 (w), 937 (s), 886 (m), 860 (w), 782 (w), 763 (m), 702 (w), 674 (w), 595 (w).^{1}H NMR (400 MHz, DMSO-d_6): 9.55 (s, 1H), 8.05 (d, $J = 8.0$ Hz, 1H), 7.87 (t, $J = 8.0$ Hz, 1H), 7.70 (t, $J = 7.6$ Hz, 1H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.49 (t, $J = 1.6$ Hz, 2H), 7.26 (d, $J = 8.0$ Hz, 1H), 6.96 (d, $J = 2.0$ Hz, 1H), 5.85 (s, 1H). Mass (ESI) found m/z: 283.0438 ($m + 1$); calculated exact mass for $C_{16}H_{10}O_3S$, 282.0351. UV (methanol), 318 nm ($\varepsilon_{methanol} = 2.78 \times 10^4$ M^{-1} cm^2).

2.2.4. Preparation of solvates of *1*

2.2.4a: Solvate **1.methanol** was obtained by crystallization of **1** from its solution in methanol. IR (KBr, cm^{-1}): 3494 (bw), 2973 (w),